Isotope Tracer Approaches for Characterizing Artificial Recharge and Demonstrating Regulatory Compliance

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ABSTRACT

Potable reuse of groundwater from waste-water origins requires new methods to quantify proposed regulatory criteria such as subsurface residence times, dilution, and water quality transitions. Isotope tracers oxygen-18 (^{18}O), tritium (^3H), dissolved noble gases, and radiocarbon (^{14}C) have been used together in Orange County to age-date groundwater, quantify mixing, and characterize changes in total organic carbon (TOC). Simultaneous measurements of ^3H and helium-3 (^3He) are used to determine groundwater ages between 1 and 40 years with uncertainties of ± one year. These ages map preferred groundwater flowpaths and identify groundwater ages of ≤1 year.

Wells recharged from the Anaheim Lake spreading basin were used to monitor arrival times and dilution of 6000 acre-ft of ^{18}O-distinct Colorado River (COR) water introduced during a controlled recharge experiment. In addition, isotopically enriched Xe was introduced into the basin to quantify COR dilution of >90%. The COR arrived at 7 wells between 30 and 200 days after recharge commenced. The COR was diluted up to 90% at distances and depths ≤1000 feet from the lake. Results suggest that dilution of 50% is obtained within 6 months from time of recharge.

^{14}C measured in TOC of Anaheim Lake bottom water (<1.0μm) was 3 pmc higher than the DOC (<0.2μm). The same water collected one month later in a nearby monitoring well, as confirmed by ^{18}O, showed a 50% reduction in TOC concentration, and a 7 pmc decrease in ^{14}C relative to the surface water. This result suggests that older carbon components increase in TOC after recharge.

INTRODUCTION

Water impoundment and diversion in the western United States under the Reclamation Act resulted in rapid urban growth and intense agricultural irrigation. Continued growth has fostered a persistent water demand leading to groundwater overdraft and decreased water quality in many urban areas. In southern California, increasing water import costs makes water reuse an attractive option. For example, advanced treatment of waste-water and intentional recharge into groundwater aquifers provides a mechanism to offset drinking water demands and to prevent irrecoverable aquifer damage due to sea water intrusion. In the western half of urbanized Orange County, California groundwater levels remain consistently below sea level. Areas of groundwater deficit have been stabilized by direct injection of recycled water near the coast, and surface spreading upgradient in the Forebay, with Santa Ana River (SAR) water. In addition, 10-25% of recharge to the Forebay is from annual purchases of Colorado River water (COR). During baseflow the SAR comprises ~100% tertiary treated waste-water discharged from upstream communities.

Proposed regulations for the potability of water of waste-water origins stipulate minimum subsurface residence times of one year, dilution of ≥50% with a non-waste-water source, and removal of TOC to a 1 mg/L level (e.g. Asano, 1993). In this report we present a combined isotope measurement approach for measuring groundwater ages to ±1 year and delineating

mixtures of recently recharged water down to ~10%. In addition, we show new data for TOC removal during recharge and present isotopic data that quantify changes in the character of the TOC. The short space and time scales and reduced uncertainties required by the proposed regulations render standard groundwater modeling approaches obsolete. The isotopic approach presented here provides the needed data for more accurate model development and calibration.

METHODOLOGY

Tritium produced by atmospheric testing of nuclear weapons in the 1960's provided a distinct and measurable signature, whose concentration in precipitation and shallow groundwater has decayed near-exponentially for the past 35 years. Tritium has an ideal half-life (12.34 years) for dating shallow groundwater, but due to spatial and temporal variations in the fallout concentration, groundwater dating from tritium alone yields large uncertainties. However, simultaneous measurements of the ^3H and the decay product stable ^3He provide a parent-daughter age-dating method that does not rely on knowing the initial ^3H concentration. Therefore, ages can be calculated from the following relationship:

$$Age = -17.9 \ x \ ln\left(\frac{^3H}{^3H + ^3He_{trit}}\right)$$

The ^3H-^3He dating method has been applied in several groundwater studies, and correction methodologies for additional helium sources such as excess air and radiogenic ^4He have been developed (e.g. Schlosser et al., 1988).

The stable isotope of ^{18}O in water varies in precipitation as function of temperature (i.e. elevation and latitude; Craig, 1961; Taylor, 1974). COR water is from Rocky Mountain watersheds and has a significantly lower ^{18}O abundance than coastal groundwater. Hence, COR recharged into groundwater of the Orange County Forebay would be strikingly different from local recharge, which provides a

conservative tracer of water molecules. The COR tracer migration and dilution is fully quantifiable with ^{18}O, which provides a framework to characterize water quality changes such as TOC reduction.

^{14}C measurements of the TOC may provide additional evidence for either selective removal of labile components in the TOC, or interaction between TOC and sedimentary organic matter (SOM). ^{14}C in atmospheric CO_2 was elevated during nuclear testing similar to ^3H, and therefore, today the surface water TOC still has residual "bomb pulse" concentrations (e.g. Schiff et al., 1997). The natural ^{14}C in SOM, however, should be much lower due to radioactive decay (^{14}C half-life is 5730 years) since sediment burial (e.g. Stevenson, 1985).

All samples were analyzed at LLNL using published methods (Epstein and Mayeda, 1953; Schlosser et al., 1988; Surano et al., 1992). The ^{18}O abundance is measured as a ratio to ^{16}O and reported in δ notation, where

$$\delta^{18}O = \left(\frac{R}{R_{std}} - 1\right)1000$$

where, R represents the $^{18}O/^{16}O$ ratio of a sample, and R_{std} is the isotope ratio of the NBS standard SMOW.

Samples for ^{14}C in TOC were collected in pre-cleaned glass bottles, poisoned in the field with concentrated $HgCl_2$, shipped and stored refrigerated. Samples were filtered at 1.0 and 0.2μm, concentrated 100X by rotary vacuum distillation, acidified with 3M HCl to remove inorganic carbon, centrifuged, and freeze-dried. Salts were vacuum sealed in quartz tubes with CuO and combusted to CO_2 at 900°C for 3 hours. CO_2 was converted to graphite using H_2 gas, a cobalt catalyst, and reaction temperature of 570°C. The ^{14}C of the graphite was measured by accelerator mass spectrometry. The $^{14}C/^{12}C$ ratios are reported as percent of modern carbon, normalized to Oxalic Acid-1, representing the ^{14}C abundance of atmospheric CO_2 in 1950.

RESULTS AND DISCUSSION

Age-Dating

Groundwater ages calculated from the ^{3}H-^{3}He measurements show a regular east to west increase consistent with inferred flow directions (Fig. 1). Average linear velocities, implied by distances between age contours, decrease with westward distance. This is anticipated since the basin increases in width and depth to the west. However, preferential flow of groundwater is implied by ages ≤ 1 year in shallow wells (<300 ft) ~2 miles southwest of the Anaheim Lake. This preferred flow is also apparent further southwest where age contours are separated by larger distances. In contrast, ~2 miles directly west of Anaheim Lake, ages up to 5 years were found in shallow groundwater, while at distances >2 miles, ages reach 20 years in a relatively short distance.

The age distribution in Figure 1 indicates that near the recharge basins, flowpaths are highly discrete. This is supported further by the distribution of groundwater ages with depth. For example, deep production wells (P-6, P-7, and P-8) screened >400 feet below Anaheim Lake yielded ages of 12 to 18 years. Likewise, a nested monitoring well (WB-3) showed ages of ≤ 1 year at 230 ft, 3 years at 460 ft, 5 years at 590 ft, and 25 years at 906 ft. Similar age increases with depth occur in various multi-point monitoring wells throughout the study area.

Groundwater ages adjacent to the SAR range from ≤ 1 to 10 years. The SAR channel is responsible for percolating nearly half the annual recharge into the Forebay, however the heterogeneity in age distribution suggests that older groundwater likely mixes with young recharge. In addition, recharge directly from the river may be highly discrete, and sampling densities are too low to identify preferred flowpaths in this area.

Since groundwater dispersion is likely very high in the Forebay, inter-aquifer mixing complicates ^{3}H-^{3}He age calculations. Mixing of two groundwaters with different ^{3}H-^{3}He ages will always produce a calculated age weighted towards the older mixing end-member, since the ^{3}H content in recharge was higher in the past. Therefore, ^{3}H-^{3}He ages calculated for groundwater residing in heterogeneous geologic media should be considered "mean" ages. For regulatory purposes, however, groundwater with ^{3}H-^{3}He ages of ≤ 1 provides the necessary evidence to identify recently recharged groundwater too young to produce. However, a mixed groundwater >1 year old that incorporates a component of recharge <1 year old will not be distinguishable from age-dating alone. Therefore, additional methods are needed to quantify young water contributions.
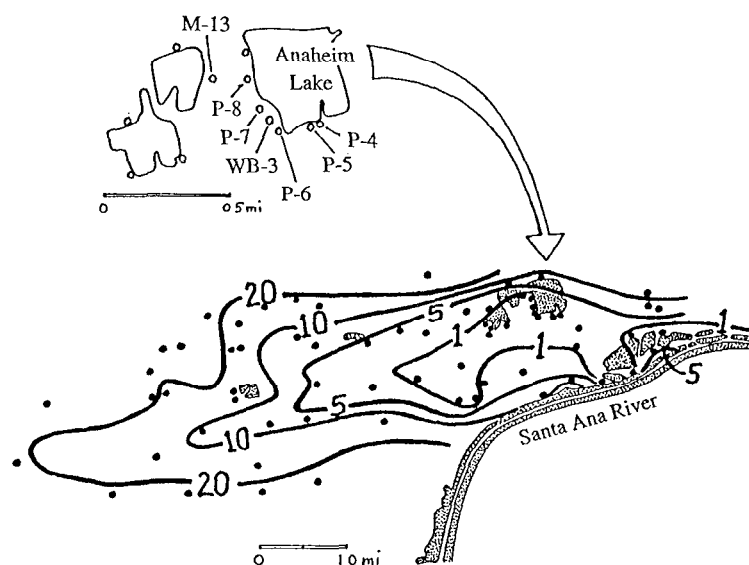

Figure 1. In the Forebay, groundwater age contours in years show increasing ages toward the west, consistent with inferred groundwater flow directions. The age distributions map preferential flow paths. For multi-depth samples, ages have been averaged.

Conservative Tracers

A controlled recharge experiment was conducted in order to trace the migration and mixing of groundwater recharge <1 year old beneath and downgradient from Anaheim Lake. Approximately 6000 acre-ft of COR water was diverted over 50 days into Anaheim Lake

beginning October 1, 1996. The lake was drained before COR was introduced. In addition, there was a paucity of COR diversions over the previous 20 months before the recharge experiment commenced. The $\delta^{18}O$ monitored in several wells during the experiment quantified arrival times and mixing of COR with groundwater from other recharge sources (Fig. 2). Approximately 11 days after the beginning of the COR diversion, 160 cm³ (at STP) of an isotopically enriched Xe tracer (50% was ^{124}Xe; natural ^{124}Xe abundance is 0.1%) was added and mixed with the COR.

The $\delta^{18}O$ value of the COR tracer is ideal since its ~4.0 per mil depletion relative to local recharge provides a large dynamic range over the analytical precision (±0.1 per mil). Therefore, mixtures as low as 10% can be calculated. Arrival of COR recharge to shallow wells (<300 ft; WB-3/1 and P-4, see Fig. 1) immediately adjacent to Anaheim Lake occurred within ~15 days after the beginning of COR diversion. Within 30 days, groundwater in these wells was ~100% COR. After ~90 days these groundwaters returned to their initial values.

Well P-5 is 100 ft from well P-4, is of the same construction, but is screened slightly deeper. The COR tracer arrived within ~15 days at P-5, but reached a maximum mixture of only 50% after 90 days. The tracer break-through curve for P-5 formed an irregular shape compared to the other well waters. The shape suggests that non-transient flow occurred, which would cause mixing proportions between different groundwaters to change over time.

Well M-13 is a shallow monitoring well 1000 feet down gradient of Anaheim Lake. The COR arrived at this well within ~100 days and was diluted by about 20%. The COR arrived at WB-3/2 (second level of WB-3, 460 ft), which is completed within a confining layer, in about 130 days and was diluted ~50%. These latter two wells demonstrate that dilution of the tracer increases with time and distance, consistent with that predicted for simple dispersion.
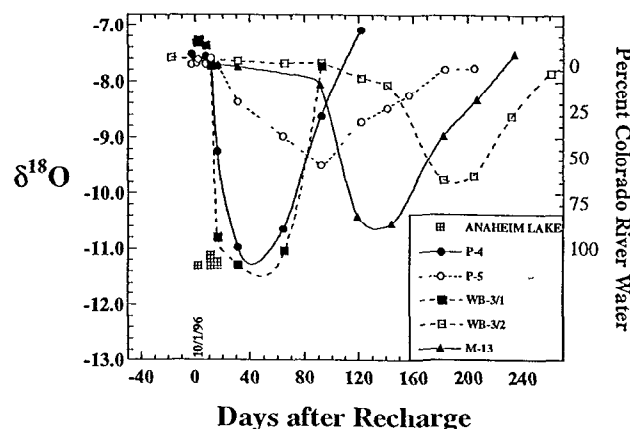

Figure 2. The $\delta^{18}O$ values of groundwater with time provide quantifiable tracer data for determining arrival times and groundwater dilution.

The ^{124}Xe tracer is ideal for quantifying mixtures below 10%, since it was added to Anaheim Lake at a concentration that essentially doubled the natural dissolved ^{124}Xe content. This provides quantification of a 99% dilution. An example of its value is shown in Figure 3, which illustrates the $\delta^{18}O$ values and $^{124}Xe/^{132}Xe$ ratios in deep production wells (screened ~400-1200 ft) adjacent to Anaheim Lake. Since the $\delta^{18}O$ values of these wells show only small variations during the recharge experiment, possible contributions from COR are difficult to interpret. Inspection of the $^{124}Xe/^{132}Xe$ ratios, however, show that well P-8 has a clear and quantifiable increase in ^{124}Xe, while the other two wells remain at natural abundances (natural $^{124}Xe/^{132}Xe$ ratio is 0.00355). The $^{124}Xe/^{132}Xe$ ratio of the spiked water is estimated at 0.0085, indicating that ~5-10% of the tracer arrived at well P-8. Closer inspection of the $\delta^{18}O$ for well P-8 reveals that a slight decrease occurred, equivalent to a 10% mixture, at the same time the ^{124}Xe increase occurred, yet the $\delta^{18}O$ alone would not have been definitive proof of COR mixing.
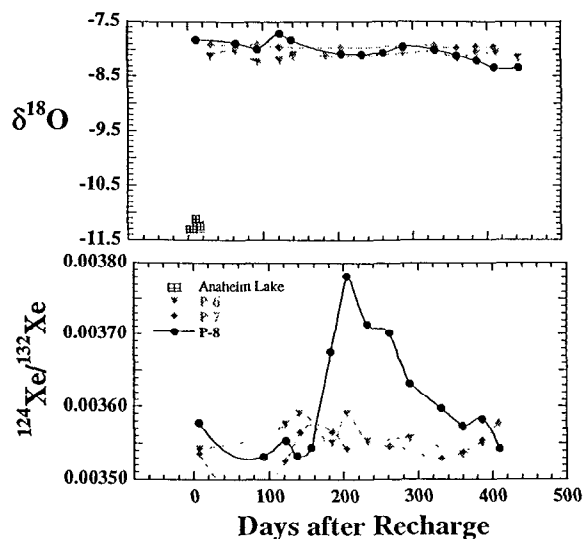
Figure 3. The $\delta^{18}O$ values of deep production wells below Anaheim Lake show small variations that can only be correlated to COR recharge when compared to the Xe isotope tracer results. In this case, the small $\delta^{18}O$ decrease in well P-8 correlates with increased $^{124}Xe/^{132}Xe$ ratios.

Tracers of Reactive Transport

TOC comprises ~90% unidentified substances (e.g. Thurman, 1985). In waste-water TOC may incorporate mutagenic compounds, which is the basis for its proposed regulation to 1 mg/L for groundwater comprising ≤50% waste-water (Asano, 1993). Studies characterizing TOC are limited by resolution in analytical methods. Studies investigating changes in the character of TOC during groundwater recharge are lacking. Below we demonstrate TOC removal during tracer recharge experiments, and infer structural changes from ^{14}C measurements.

TOC removal was quantified in two separate recharge experiments (Table 1). In the October experiment, TOC of COR in Anaheim Lake was at 3.0 mg/L. One month later when this same water mass was sampled from well P-4, as confirmed by $\delta^{18}O$ values, the TOC was 1.5 mg/L. The measurements were repeated in February and March, 1997. This time SAR water was in Anaheim Lake. The high TOC content of SAR likewise was decreased by ~50% during recharge when sampled one month later in well WB-3/1.

Table 1

Sample	Sample Date	TOC mg/L
Ana. Lake	10/1/96	3.0
P-4	10/31/96	1.5
Ana. Lake	2/18/97	8.4
WB-3/1	3/17/97	4.1

The ^{14}C content of the TOC was measured in Anaheim Lake water at different depths in February, and in well WB-3/1 in March (Fig. 4). For the surface water samples, the ^{14}C of the TOC filtered at 1.0μm showed no significant variation with depth. However, the ^{14}C content of the 0.2μm filtrate at the middle and bottom layers were 3 pmc. For the groundwater sample, the ^{14}C of the TOC was up to 7 pmc lower than the surface water. However, the $\delta^{13}C$ values of the TOC for the surface water and groundwater samples showed no difference. In addition, the TOC concentrations in the surface water for both size fractions showed an increase from ~5.0 ±1.0 mg/L at the surface to ~7.0 ±1.0 mg/L near the bottom.
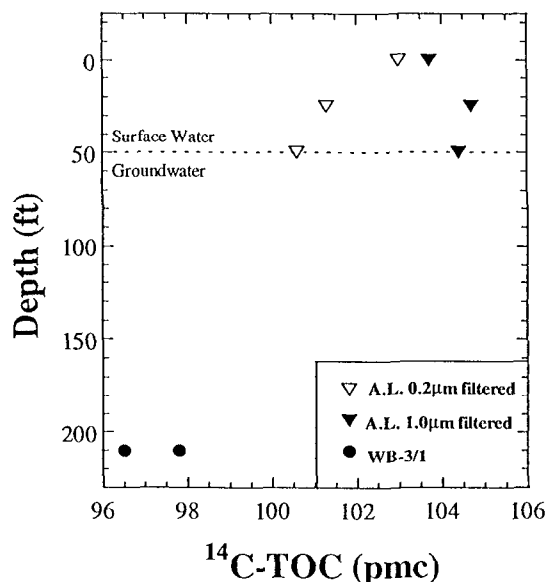

Figure 4. The ^{14}C content in TOC decreases during recharge, either due to selective breakdown of younger, more labile components, or from interaction with older, sedimentary organic matter. Precision in ^{14}C measurements is ±1 0 pmc.

The increased TOC concentrations with depth indicate that organic carbon accumulates toward the bottom of the lake. The concentration of humic substances is known to increase with depth in lakes, and have been proposed to originate either from iron oxide precipitation or from anaerobic decomposition of particulate detritus (e.g. Steinberg and Muenster, 1985). The TOC increase in Anaheim Lake was associated with a ^{14}C decrease in only the 0.2μm filtrate, while the ^{14}C of the 1.0μm remained the same, although as noted above, both sizes increased in total concentration. The increased TOC in the smaller size, however, is preferentially composed of older organic material, and this is consistent with formation of smaller molecules from decomposition of older SOM (Steinberg and Muenster, 1985). However, this doesn't explain why the 1.0μm filtrate also increased in concentration.

Assuming that the lower ^{14}C in TOC of the groundwater was due entirely to exchange with SOM, a mass transfer can be calculated. The ^{14}C of the SOM was not determined. However, a lower limit of 25 pmc is a reasonable estimate considering the depth of the monitoring well and the <10,000 year age of the sediments (R. Herndon, Orange County Water District, personal communication). Using the ^{14}C of the 0.2μm filtrate at the bottom of the quarry (101 pmc) as the beginning concentration, and 25 pmc as the SOM concentration, then obtaining the 97 pmc observed in the groundwater would required only a 5 percent mass transfer of SOM into the TOC. Using the 1.0μm filtrate as a beginning ^{14}C content, then a 9 percent mass transfer is required. A larger mass transfer would be required if the SOM were actually greater than 25 pmc.

Further work is required to better understand these data. In particular, ^{14}C measurements on the SOM are needed. However, it cannot be ruled out that the ^{14}C decrease of the TOC is simply caused by selective decomposition of younger, more labile carbon components of the TOC during recharge. In this case, more refractory parts of the TOC may be composed

of older carbon. This hypothesis is testable by measuring the ^{14}C of humic substances separated from the TOC. Likewise, ^{14}C measurements on products of weak oxidation and other selective decomposition methods may provide further information. In addition, ^{14}C measurements on TOC in groundwater >1 year old would indicate if ^{14}C in TOC continues to decrease along a flowpath, away from the point of recharge.

SUMMARY

For regulatory compliance in groundwater reuse projects, isotopic measurements of ^{3}H and ^{3}He provide a method for determining groundwater age 1-40 years and for mapping preferential groundwater flowpaths. Mixing of groundwater <1 year old with older groundwater requires the use of additional tracers and real-time monitoring for transit times and dilution. The stable isotopes of water and isotopically enriched noble gases are ideal conservative tracers of water mass transport. The ^{14}C content of TOC shows promise for quantifying carbon mass transfer to and from TOC in recharged groundwaters.

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